

### Theoretical Determination of Electron Density in Organic Molecules

IN a recent paper, Abrahams, Robertson and White<sup>1</sup> have determined the electron density in naphthalene by means of X-ray analysis. They found that the electron density is greatest at the carbon atom in the meso-position, smallest at the  $\beta$ -position, and intermediate at the  $\alpha$ -position. Between each pair of carbon atoms there is an electron density, evidently due to the binding pairs, which assumes its largest value between the  $\alpha$ - and  $\beta$ -positions, and the smallest value between the two meso-positions.

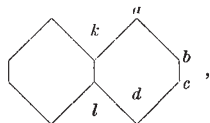
It may be of interest to note that precisely these results can be derived, at least qualitatively, from the theory of the chemical bond. I have used the method first applied by Heitler and Rumer<sup>2</sup> for determining the wave function of naphthalene in the zeroth approximation. Starting from a set of independent pure valence states, the energy can be calculated in terms of the well-known exchange integrals (by solving the corresponding secular equation), and hence the corresponding linear combination of pure valence states can be obtained.

Knowing the wave function, the calculation of the electron density is straightforward and follows the same pattern as that of the energy. If  $u_a, u_b$  are the wave functions of the valence electron in the atoms  $a$  and  $b$ , then the electron density depends on two types of integral:

$$\int |u_a(1)|^2 d\tau, \quad \int u_a^*(1) u_b^*(2) u_a(2) u_b(1) d\tau. \quad (1)$$

Each occurs with certain algebraic coefficients arising from the solution of the secular problem. The first integral in (1) gives rise to an electron density at  $a$ , the second also to an *exchange density* between  $a$  and  $b$ . Values for these integrals can be estimated from the analogy of the hydrogen molecule, but the qualitative results depend on the valence structure of the molecule alone.

Carrying out this analysis, and taking into account only the interaction between neighbouring atoms, the following results are found. We denote the atoms in naphthalene as in the accompanying formula,



the electron density in  $a$  by  $\rho_a$ , the density between  $a$  and  $b$  by  $\rho_{ab}$ , etc. Then

$$\rho_h > \rho_a > \rho_b, \quad \rho_{ab} > \rho_{bc} > \rho_{ak} > \rho_{kl}.$$

All exchange densities  $\rho_{nm}$  are smaller than the  $\rho_n$ . The results are qualitatively in perfect agreement with the above experiments.

Attempts in a similar direction have been made by Daudel and Pullman<sup>3</sup>; but their results are not quite consistent because they depend on the choice of the independent basis of valence diagrams. This is not the case in our method.

Details will be published in the *Helvetica Chimica Acta*. I wish to thank Prof. W. Heitler for his advice and guidance, and the Stiftung für Stipendien auf dem Gebiete der Chemie for a grant.

O. KLEMENT

Universities of Fribourg and Zurich.  
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<sup>1</sup> *Acta Cryst.*, **2**, 238 (1949).

<sup>2</sup> "Hdb. Radiologie", Bd. VI/2, 2 Aufl. (1934).

<sup>3</sup> *J. Phys.*, **7**, 59, 74, 105 (1946).

### Ferromagnetic Resonance Absorption and a New Transition in NiOFe<sub>2</sub>O<sub>8</sub> at Low Temperature

MICROWAVE absorption phenomena, similar to those reported by Bickford for magnetite<sup>1</sup>, have been observed for nickel ferrite in measurements at a wave-length of 3.2 cm. made from room temperature down to  $-195^\circ\text{C}$ . At the lowest temperatures, two absorption peaks were obtained at 1,490 Oe. and 200 Oe., the latter gradually decreasing with rising temperature and finally disappearing at about  $-120^\circ\text{C}$ . The value of  $g$  and the maximum absorption increase with decreasing temperature. An anomaly in the magnetization, similar to that found by Weiss and Forrer for magnetite<sup>2</sup>, was observed in the range  $-120^\circ$  to  $-195^\circ\text{C}$ ., where the magnetization falls suddenly by an amount which is the smaller, the higher the field. Similarly, the electrical resistivity rises suddenly in the same range. These phenomena may be due to a transition between  $-120^\circ$  and  $-195^\circ\text{C}$ .

Experiments at temperatures below  $-195^\circ\text{C}$ . are being planned.

I wish to express my thanks to Dr. T. Muto of the University of Tokyo for his valuable suggestions, and also to Mrs. Y. Torizuka, J. Simoizaka, Y. Kojima and Miss K. Takahashi for their assistance during the course of the experiments. Detailed results of the present work will be published in *Sci. Rep. RIU*.

TOSHIKO OKAMURA

Research Institute for Scientific Measurement,  
Sendai, Japan.

<sup>1</sup> Bickford, L. R., *Phys. Rev.*, **78**, 449 (1950).

<sup>2</sup> Weiss, P., and Forrer, F., *Ann. de Phys.*, [10], **12**, 279 (1929).

### Volume Rectification in Zincite

THE experiments of Khastgir and Das Gupta<sup>1</sup> showed that when carborundum, zincite or silicon was placed between two mercury electrodes giving large contact areas, there was considerable rectification, while similar experiments with symmetrical crystals like iron pyrites, magnetite, galena, etc., showed no rectification when the surface effects were eliminated. These experimental results suggested that the rectification observed in polar crystals such as carborundum, zincite or silicon with electrodes of large contact-areas should be associated with the asymmetry in the structure of these crystals. The experiments of Deaglio<sup>2</sup> with two different thicknesses of carborundum having the same contact-areas on the opposite faces, mechanically scraped plane and platinized, showed that rectification per centimetre thickness, as indicated by the static characteristic curves, was the same. This proved that the observed rectification in carborundum was definitely associated with the volume of the crystal and not with the area in contact with the electrodes. The object of the present communication is to report some experimental results with zincite, which has shown similar rectification depending on the volume of the crystal. A theoretical treatment is also given of the origin of volume rectification in polar crystals.

The zincite crystal cut in the form of a cube was mounted between two plane electrodes of large contact area pressed tightly against the opposite faces. Having applied a constant radio-frequency voltage